Nitrogen isotope of chloropigments in the nitrogen cycle in the ocean

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Chloropigments (chlorophyll *a* and pheophytin *a*) are nitrogeneous compounds preserved in the sediments for long time. As directly involved in phytosynthetic process, isotope analysis of chloropigments provides a "to the point" information to understand biogeochemical processes in the surface water [1]. In this study, nitrogen isotopic compositions ($\delta^{15}N$) of chloropigments ($\delta^{15}N_{chl}$) and nitrate ($\delta^{15}N_{NO3}$) were determined to investigate the nitrogen cycle in the photic zone. Particles and water samples were collected from western North Pacific (Station K2, 47◦00'N, 160◦00'E) during summer blooms. The chloropigments were extracted and purified by HPLC, and $\delta^{15}N_{chl}$ was determined by a nano-EA/IRMS [2], which is capable of determining $\delta^{15}N$ of as small sample as 1.5 nano molar of chloropigments.

We observed $\delta^{15}N_{chl}$ of -10.5 to +1.9‰ and $\delta^{15}N_{NO3}$ of +6.6 to +9.9‰. Based on the equation between $\delta^{15}N$ of phytoplankton ($\delta^{15}N_{phy}$) and $\delta^{15}N_{chl}$ ($\delta^{15}N_{phy} \approx \delta^{15}N_{chl} + 4.8$ [3][4]), the isotopic defference from phytoplankton to nitrate was estimated to be -8 to -13‰. The range is greater than expected values of -5 to -10‰ [5]. The large difference were potencially explained by either (1) large isotopic fractionation during nitrate assimilation by phytoplankton, or (2) significant contribution of ammonia as a substrate for the photosynthetic nitrogen assimilation. We applied a nitrogen cycle modell in the surface ocean [5] to these data set, and concluded the large (>50%) contribution of ammonia as a substrate for the phytoplankton. Since chlorophylls are also preserved in the sediment traps and suried in the sediments for long, this method provides powerful tool to study nitrogen cycle in the paleo-environments.

[1] Ohkouchi & Takano (2013) *Treatise on Geochemistry 10: Organic Geochemistry* pp.251 [2] Ogawa *et al*. (2010) *Earth, Life, and Isotopes*. pp.339 [3] Sachs *et al*. (1999) *GCA* **63**, 1431–1441 [4] Ohkouchi *et al*. (2006) *Biogeosci* **3**, 467-478. [5] Yoshikawa *et al*. (2015) *J Oceanogr* doi:10.1007/s10872-015-0308-2.